Kinetics & Rate Laws

Intro to Rate Laws

- rate law: means by which we can relate the rate of a chem rxn to [reactants]
- the rate law for a rxn is dep. on the specifics of how a rxn proceeds called the mechanism
  - what bonds break first; form first, any intermediate chem species
- determ. rate law for a rxn → gain insight into potential mechanisms
  - ↳ connect macroscopic w/ microscopic/mc ideas
- **chem. kinetics**: study of rates of chem. change
- look @ [a T to see what aff. rxn to explain how bonds broken/made
- helps max. rate form products once you know mech. + what to manipulate

Reaction Rates

- rate of a chem. rxn is a measure of how fast the rxn is proceeding.
  - measure of Δ in C of chem. species as a fxn of time
- [react] + [prod] relat. by balanced chem. eq. → relate Δ to the coefficients

Ex/ $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ (ammonia)

- rate consumption of N_2 gas is related to the rate of form. of NH_3 gas
- for each mole N_2 consumed, 2 moles NH_3 formed → rate form NH_3 will be 2x rate loss N_2

$$\frac{-\Delta[N_2]}{\Delta t} = \frac{+\Delta[NH_3]}{2\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} = \text{rate}$$

- $\Delta[N_2]$ for same period time = $\Delta[NH_3]$ for the same period time ÷ 2 (b/c happening 2x as fast)

$$\frac{-d[N_2]}{dt} = \frac{+d[NH_3]}{2dt} = \frac{-d[H_2]}{3dt} = \text{rate}$$

- take deriv b/c above = for tiniite period of time

unit: M/s or Ms^{-1} (Molarity per second) b/c Δ concentration/time

- doesn't really work when there are intermediate steps and products

Factors Affecting Rates

- 4 categories

① medium: physical state of the reactants since rate dep. on details of the rxn mech.
  - Ex/ aside iron rusts more quickly than inside b/c more exposed to O_2

② concentration: way C aff. rate tells us a lot about how rxn is happening (mech.)
  - relat. how rate + C = rate law: measured experimentally since can't be determ. by looking @ a balanced eq.

③ temperature: important b/c typically there is an E barrier b/w react. + prod.
  - means b4 you make any new bonds of products, need to break bonds in react. or form some intermediate cmpd that are usually higher in E
  - only mlcs w/ sufficient E will react → @ higher T, more mlcs will have sufficient E
  - ↳ nearly all rxns have faster rate @ higher T

④ catalyst: catalyst is a cmpd. that Δ reaction mech → allow to proceed @ a faster rate
  - is part of the rxn mech but is not consumed during the chem rxn and doesn't appear as a react. nor prod.
  - role = lower E barrier b/w react. + prod. allowing rxn to proceed @ faster rates @ lower T

Empirical Rate Laws

rate laws for an overall chem rxn cannot be deduced from the written rxn but must be determ from experiments (this the name "empirical")

- rate law relates rate of rxn to C_{react}

Ex/ $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ has the rate law: rate $= k[NO_2]^2$

- this rxn is second order bc dep on $[NO_2]^2$
- is zeroth order in CO since dep on $[CO]^0$ aka doesn't dep on [CO]
- k = rate constant
- overall order = 2 = sum of all orders of the reactants (2+0=2)

- rate laws will always have the same form: rate $= (k)(C_{react})^{power}$ units: Ms^{-1}
  - ↳ rate constant will have whatever units necessary to make Ms^{-1}
- usually only 0th-2nd order

Ex/ 1st order: rate $= kC_{react}$ so $k =$ [redacted] s^{-1}

2nd order: rate $= k(C_{react})^2$ so then $k =$ M

Determining Rate Laws

- run series of experiments w/ diff initial conditions + compare the very initial rate of rxn to avoid measuring backward rxns + since rate Δs over time
- by $\Delta C_{initial}$ we can see what C aff rate + in what way

Ex/ $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Experiment	initial $[NO_2]$ (M)	initial $[CO]$ (M)	initial rate (Ms^{-1})
1	5×10^{-4}	1.6×10^{-2}	2.8×10^{-9}
2	5×10^{-4}	3.2×10^{-2}	2.8×10^{-9}
3	1.5×10^{-3} (inc by factor of 3)	3.2×10^{-2}	2.5×10^{-8} (inc by factor of 9)

rate Δs when $[NO_2]$ Δ

$[NO_2]$ inc x3 → rate inc x9 → know is $[NO_2]^2$ bc $9 = 3^2$

now know rate $= k[NO_2]^2$

solve for k $\quad k = \dfrac{2.8 \times 10^{-9}}{(5.0 \times 10^{-4})^2} = 0.011\ M^{-1}s^{-1}$

- is 2nd order → must involve some bimolecular step that involves collision b/w 2 NO_2 mlcs bc based on second order NO_2
- can't about rate laws bc give us insight into mech of rxns